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(54) Process for the manufacture of methyl mercaptan

(57) Methyl mercaptan is obtained by reacting a carbon oxide, hydrogen and hydrogen sulfide (or elemental sulfur) in the vapour phase in the presence of a catalyst which comprises a single-phase solid supported catalyst prepared by mixing an oxide, sulfide, hydroxide or salt of a metal from the group of iron, nickel, chromium, cobalt, molybdenum and zinc with either an organic amine base or an alkali metal inorganic base that is an oxide, hydroxide, sulfide or salt, and then sulfidizing the admixture.

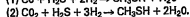
SPECIFICATION

Process for the manufacture of methyl mercaptan

5 This invention relates to the manufacture of methyl mercaptan.

Methyl mercaptan is a well known article of commerce, being used as an intermediate for the manufacture of a variety of agricultural chemicals, and as a raw material for the manufacture of methionine, a widely used feed supplement for poultry. The current preferred commercial method for manufacturing methyl mercaptan is by reaction of methanol and hydrogen sulfide. A variety of catalysts can be used such as thorium, 10 zirconia, activated aluminas, silica-aluminas, and alumina promoted with tungstates or molybdates (U.S. Patent 2,820,062) or with heteropoly acids or their salts (U.S. Patent 3,035,097). These processes as practiced commercially are highly efficient and provide methyl mercaptan in high yield and purity.

Nevertheless, further economy can be achieved by the use of the more basic raw materials carbon monoxide or carbon dioxide in place of methanol. Methyl mercaptan can be prepared from carbon oxides 15 according to the following equations:



20 U.S. Patent No. 3,070,632 discloses the prior art process associated with equations (1) and (2) above. However, this method has a number of shortcomings from a commercial viewpoint. The yields are rather low. The most favourable yield for methyl mercaptan is in Example 2 of the above patent and is 23.2%. The two phase catalyst system is a complex system involving a large amount of powdered sulfidative hydrogenation catalyst suspended in a large volume of a liquid organic amine, relative to the amount of 25 reactants employed. The preferred reaction conditions disclosed are inherently expensive from a commercial viewpoint as they involve operating at high pressures within the 1200 to 2000 psig. range over long reaction times of 3 to 6 hours.

In addition, the amine co-catalyst of the prior art method procudes hydrosulfide salts at the reaction conditions and these salts are unstable at standard atmospheric conditions, whereby highly toxic hydrogen 30 sulfide gas is released. The yield is particularly low with respect to utilizing carbon dioxide as the raw material, as shown in the aforementioned equation (2). Example 1 of the above patent shows carbon monoxide produces a yield of 17.7%. Less than 5% conversion is obtained with carbon dioxide.

The present invention seeks to overcome these shortcomings and provides a practical and economical process for the production of methyl mercaptan from carbon oxides.

35 In accordance with this invention there is provided a process for the manufacture of methyl mercaptan which comprises continuously feeding to a reactor a vapour phase reactant mixture comprising a carbon oxide, hydrogen and either hydrogen sulfide or elemental sulfur, contacting the reaction mixture, in the vapour phase and at an elevated temperature and pressure with a hydrogenation catalyst, recovering from the reactor a gaseous product stream, and separating from the product stream the product methyl 40 mercaptan, wherein there is used a single phase solid catalyst prepared by:

A. mixing:

(1) an oxide, sulfide, hydroxide or salt of a metal or metals selected from iron, nickel, chromium, cobalt, molybdenum or zinc with

(2) at least one compound selected from

45 (a) organic amine bases, namely aliphatic, cycloaliphatic, saturated heterocyclic, and aromatic amines having greater than 6 carbon atoms in each aliphatic, cycloaliphatic or aromatic radical, and

(b) alkali metal inorganic bases, namely alkali metal oxides hydroxides, sulfides and salts; and then

B. at least partially sulfiding the admixture of A by heating the admixture in the presence of hydrogen sulfide or elemental sulfur; with the proviso that step B is optional when components A(1) and A(2) both comprise a 50 metal sulfide.

The use of the foregoing single phase solid catalyst provides enhanced conversions with lower reaction times at lower temperature and pressure conditions, without the formation of substantial undesirable by-products.

Broadly speaking the catalyst used in this invention is a conventional hydrogenation catalyst treated with 55 an organic or inorganic base and sulfided with hydrogen sulfide at elevated temperatures.

The organic base, component A(2)(a), may be any high molecular weight amine of sufficiently high boiling point so as not to volatilize from the catalyst surface at an appreciable rate at the process conditions. The amine may be primary, secondary or tertiary and may be aliphatic, cycloaliphatic, aromatic or a saturated heterocyclic amine. A preferred example is tridodecylamine.

60 The inorganic base, component A(2)(b), may be any alkali metal oxide, sulfide, hydroxide or salt, but is preferably an oxide, sulfide, hydroxide or salt of potassium, rubidium or cesium, with cesium being especially preferred. It is understood that on treatment with H_2S these bases are at least partially converted to the hydrosulfides and/or sulfides.

The hydrogenation catalyst, component A(1), may comprise iron, nickel, chromium, cobalt, molybdenum 65 or zinc, singly or in combination as their oxides, sulfides, hydroxides or salts alone or on a suitable support

such as alumina, silica, kieselguhr, carbon, clays or refractory materials. Although oxides, hydroxides and salts of the hydrogenating metal may be used, it will be understood that the hydrogenating metals are at least partially converted to the sulfides on treatment with H_2S . A preferred hydrogenating metal is nickel with nickel oxide being the preferred pre-sulfided form. Also preferred are catalyst compositions containing zinc as the hydrogenating metal, especially in combination with chromium, e.g. as zinc chromite.

The preferred support material is activated alumina used in an amount of from 10–90% by weight of the total catalyst system.

In the preparation of the catalyst, the promoter, component A(2)(a) and/or A(2)(b), is preferably used in an amount of from 5 to 30% by weight, with the hydrogenation catalyst correspondingly providing 95 to 70% by weight of the catalyst mixture.

The most preferred catalyst composition contains about 5% by weight cesium sulfide and 13% by weight nickel sulfide supported on activated alumina. In a typical preparation 950 grams of a commercial pelletized hydrogenation catalyst containing 11% nickel oxide on activated alumina (Harshaw Ni-0301 T) is predried at 150°C and impregnated with a solution containing 50 grams of cesium hydroxide in 250 cc of water. The solution is added slowly with thorough mixing and the wet catalyst is dried overnight in an oven at 150°C.

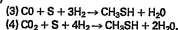
The dried catalyst is charged into the process reactor and sulfided by passing hydrogen sulfide gas over it at about 370°C and atmospheric pressure for several hours (e.g. 6–8 hours) until water of reaction is no longer present in the effluent gas stream. The catalyst is now ready to use in the process.

The process is preferably operated in a continuous fashion by preheating and premixing the reactant gases carbon monoxide or carbon dioxide, hydrogen sulfide, and hydrogen, and passing the mixture over the catalyst bed under appropriate conditions for reaction to occur. The ratio of reactants to be used is based on the stoichiometry of equations (1) and (2). Preferably the carbon oxide will be reacted with a molar excess of hydrogen sulfide and a molar excess of hydrogen. Most preferably, molar ratios of $CO_{1-2}/H_2S/H_2$ between 1/3/2 and 1/8/8 are used. The gases are preheated to about 180–300°C, mixed and passed through the catalyst bed to effect reaction.

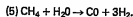
The hydrogen sulfide reactant can be prepared *in situ* within the reactor by feeding elemental sulfur to the reactor, in which case the molar ratio of carbon oxide, elemental sulfur and hydrogen with respect to one another charged to the reactor is within the range of about 1/3/3 to about 1/8/10.

A wide range of reaction conditions may be used to obtain conversion to methyl mercaptans. In general the production of methyl mercaptan is favoured by higher pressures up to about 600–1000 psig (4137–6894 kN/m²), catalyst bed temperatures in the range 250–350°C, and space velocities ranging from about 5 to 200 litres of carbon oxide per litre of catalyst per hour. Methyl mercaptan formation is also favoured by longer catalyst contact times, i.e., lower space velocities, but in commercial practice where high production rates are desired, this process can be operated at higher space velocities in the range of 60–200 litres of carbon oxide per litre of catalyst per hour with relatively high conversions of carbon oxide to methyl mercaptan per pass. The unconverted reactants can be separated by distillation from the products and recycled in a commercial operation to obtain maximum economy in raw materials.

Carbon monoxide is more reactive than the dioxide in this process and is the preferred raw material for operation with high conversions at the higher space velocities. Elemental sulfur may be substituted for the hydrogen sulfide in the process, since the hydrogen present in the feed mixture will convert the sulfur to hydrogen sulfide *in situ* at the process conditions. Correspondingly higher ratios of hydrogen must of course be used when elemental sulfur is substituted for hydrogen sulfide, the preferred molar ratios of $CO_{1-2}/S/H_2$ ranging from about 1/3/3 to about 1/8/10. The equations for the reactions with elemental sulfur are as follows:



Carbon monoxide-hydrogen mixtures can be inexpensively produced from methane and steam by the well known 'synthesis gas' process,



By adding hydrogen sulfide or elemental sulfur to 'synthesis gas' a suitable low cost reactant mixture is obtained to produce methyl mercaptan by this process.

The invention is illustrated by the following examples.

Example 1

A series of organic (amine) and inorganic (alkali and alkaline earth hydroxides and salts) basic promoters are evaluated at 5% by weight on a commercial 11% nickel oxide on alumina catalyst (Harshaw Ni-0301T) using a fixed bed, tubular, continuous reactor. The reactants are carbon monoxide, hydrogen sulfide and hydrogen. The initial nickel oxide-alumina catalyst has a surface area of 64 sq. meters per gram, a pore volume of 0.32 cc per gram, average bulk density of 70 lbs per cu. ft (1.12 gm/cc) tableted in 1/8 inch tablets. The reactants are mixed just prior to being passed forward through the vertically mounted reactor, with no

preheating. Conversions to methyl mercaptan are relatively low due to lack of preheating and the lower pressure employed (175 psig:1206 kN/m²), but the data serve to compare the effectiveness of the various basic promoters. Carbon dioxide is a major by-product at the low pressure. The pressure is controlled by an automatic back-pressure regulator, and the crude product stream is passed as a vapour through heated lines at atmospheric pressure into the gas sampling device of a gas chromatograph for analyses. The single-pass conversions and yields of carbon monoxide to methyl mercaptan (MM) are calculated from the gas chromatographic analyses.

The yield figures take into account only the unreacted carbon monoxide remaining in the crude product after a single-pass through the reactor and do not include by-products such as carbon dioxide, carbonyl sulfide, and carbon disulfide which can in fact be recycled to produce additional MM, with high ultimate yields.

The reaction conditions, conversions and yields to MM are shown in Table 1 below. All runs are of at least 15 hours duration. All catalysts are presulfided by passing hydrogen sulfide gas over them at about 370°C and atmospheric pressure for about six hours.

TABLE 1						
Catalyst Promoter (% on NiO/Al ₂ O ₃)	cc space velocity (1)	Cat. bed temp. °C	Pressure kN/m ²	CO/H ₂ S/ Molar ratio	Avg. % Conver- sion CO→MM	Avg. % Yield CO→MM
None	5	278	1206	1/4/4	20	24
(C ₂ H ₅) ₃ N	5	275	1206	1/4/4	32	34
(C ₂ H ₅) ₃ N	5	275	1206	1/8/4	36	38
Na ₂ CO ₃	5	275	1206	1/8/4	25	33
NaOH (2)	5	275	1206	1/8/4	30→16	36→32
KOH	5	275	1206	1/8/4	40	41
K ₂ CO ₃	5	280	1206	1/8/4	39	41
K ₂ WO ₄	5	280	1206	1/8/4	37	38
K ₂ CO ₃	5	284	1206	1/8/4	35	38
K ₂ CO ₃	5	288	1206	1/8/4	39	40
K ₂ CO ₃	5	285	1206	1/8/4	38	41
K ₂ CO ₃	5	285	1206	1/8/4	36	39
K ₂ CO ₃	5	282	1206	1/8/4	43	44
K ₂ CO ₃	5	287	1206	1/8/4	44	45
K ₂ CO ₃	5	290	1206	1/8/4	46	47
K ₂ CO ₃	5	293	1206	1/8/4	11	18

- (1) Space velocity: litres CO per litre catalyst per hour at standard temperature and pressure.
 (2) Conversion and yield decreased with time.
 (3) KPT: potassium phosphotungstate.

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Example 2

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Following up on the results of Example 1 and using the same operating procedure and general reaction conditions (175 psig; 1206 kN/m²), various levels of cesium hydroxide promoter on the 11% nickel oxide on alumina catalyst (Harshaw Ni-0201T) are investigated. All catalysts are presulfided. All experiments are carried out at a space velocity of 5 litres CO/litre catalyst/hour, a CO/H₂S/H₂ molar feed ratio of 1/8/4, and 175 psig (1206 kN/m²) pressure. The results are given in Table 2 below and show the 5% cesium hydroxide on NiO/Al₂O₃ catalyst to give optimum conversion to MM. The conversions and yields for this and succeeding Examples are calculated in the same manner as in Example 1.

15

TABLE 2

15

20 Catalyst	Catalyst Temp.°C	Avg. % Conversion CO→MM	Avg. % Yield CO→MM	20
1% CsOH on NiO/Al ₂ O ₃	288	31.0	34.2	
2.5% CsOH on NiO/Al ₂ O ₃	286	37.8	40.4	
25 5% CsOH on NiO/Al ₂ O ₃	290	46.9	47.6	25
10% CsOH on NiO/Al ₂ O ₃	290	39.8	42.5	
30 "	302	43.7	45.2	30
"	313	44.5	45.7	
"	318	45.4	47.3	
35 "	331	44.6	45.4	35

Example 3

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Various 5% alkali hydroxide-promoted metal oxide hydrogenation catalysts are evaluated using the same operating procedure and reaction conditions as in Example 2. All catalyst are presulfided. The results are shown in Table 3 below.

40

45 TABLE 3

45

Catalyst	Catalyst Bed Temp.°C	Avg. % Conversion CO→MM	Avg. % Yield CO→MM	
50 5% KOH on Co-Mo/Al ₂ O ₃ ⁽¹⁾	289	15	18	50
5% CSOH on CoO/Al ₂ O ₃ ⁽²⁾	288	17	19	
55 5% KOH on NiO/Kieselguhr ⁽³⁾	283	3	11	55
5% KOH on Al ₂ O ₃ ⁽⁴⁾	282			
5% CSOH on Ni-Co-Mo/Al ₂ O ₃ ⁽⁵⁾	288	17	17	

60

(1) CoMo/Al₂O₃: HDS-6A (American Cyanamid)

(2) CoO/Al₂O₃: G-67 (Girdler)

(3) NiO/Kieselguhr: HSC-102 (Houdry)

(4) Al₂O₃: H-151 (Alcoa)

65 (5) Ni-Co-Mo/Al₂O₃: G 76 (Girdler)

60

65

Example 4

High conversions and yields of carbon monoxide to methyl mercaptan are obtained by preheating the reactants and carrying out the reaction at higher pressures above 400 psig (2758 kN/m²). At the higher pressures, the CO is converted to more MM at the expense of by-product CO₂. It is believed that the CO₂ arises from the reaction of starting material CO with reaction by-product H₂O according to the well known reaction, CO + H₂O → CO₂ + H₂. The CO₂ apparently reacts slowly with H₂S and H₂ (according to equation 2) at low pressures, but much more rapidly at higher pressures. Pressures above about 700 psig (4826 kN/m²), however, are not necessary to obtain high conversions to MM as shown by the results in Table 4 below, 10 using 5% KOH on NiO/Al₂O₃ and 5% CsOH on NiO/Al₂O₃ catalysts prepared from Harshaw's Ni-0301T NiO/Al₂O₃ and presulfided at 370°C and atmospheric pressure for about six hours with hydrogen sulfide, prior to use. 10

TABLE 4

15 Pres- sure psig.	Pres- heater temp., °C	Cat. bed temp., °C	CO Space Velocity	CO/H ₂ S/H ₂ Molar Ratio	Avg. % Conv. CO→MM	Avg. % Yield CO→MM	15
20 5% KOH on NiO/Al ₂ O ₃ Catalyst							20
400	100	275	5	1/8/8	43.4	50.4	
1000	100	282	5	1/8/8	64.6	66.8	25
25 700	100	292	5	1/8/8	62.8	64.6	
600	100	290	5	1/8/8	52.0	54.9	
30 700	100	291	5	1/8/8	62.0	63.8	30
400	100	292	5	1/8/8	56.7	57.7	
1000	100	292	5	1/8/8	63.7	66.2	35
35 700	100	285	5	1/8/8	76.1	77.6	
700	300	292	5	1/8/8	82.6	83.3	
40 700	300	290	10	1/8/8	59.5	62.0	40
700	300	290	5	1/8/4	86.3	86.5	
5% CsOH on NiO/Al ₂ O ₃ Catalyst							
45 700	300	290	5	1/8/4	90.2	90.2	45

Example 5

As the CO space velocity is increased, the conversion to MM decreases and the amount of by-product CO₂ increases. It is found beneficial for high conversions at higher space velocities to use less of a molar excess of H₂S and H₂ over CO in the feed mixture and slightly higher catalyst temperatures. The data in Table 5 show that fairly high conversions of CO to MM are obtained at commercially practical space velocities in the range 50 of 60 to 180 litres of CO per litre of catalyst per hour. The major by-product at the higher space velocities is CO₂, which (as shown in the following Example 6) can be recycled to produce additional MM, or can be 55 reconverted to CO by a well known reaction with methane, CO₂ + CH₄ → 2CO + 2H₂, or other means, to provide high ultimate yields of MM.

The catalyst used in these experiments is 5% by weight CsOH impregnated on a commercial 11% NiO/Al₂O₃ 60 (Harshaw Ni-0301T) catalyst and presulfided with hydrogen sulfide as described previously.

TABLE 5

CO Space		CO/H ₂ S/H ₂	Catalyst	Pressure	Avg. %	
5 velocity		molar ratio	Temp., °C	kN/m ²	Conversion	5
					CO	MM
10	5	1/8/4	275	4826	89	10
	60	1/8/4	275	4826	54	
	60	1/6/2	275	4826	61	
15	60	1/4/2	275	4826	57	15
	60	1/3/2	275	4826	54	
20	120	1/6/2	299	4826	53	20
	180	1/8/3	316	4826	49	

25 Example 6

Carbon dioxide, hydrogen sulfide and hydrogen streams are separately preheated at 150–190°C, mixed, and passed continuously into a horizontal reactor containing a 5% by weight cesium hydroxide-promoted NiO/Al₂O₃ catalyst (Harshaw's NI-0301T) at 260–295°C. The pressure in the reactor is maintained at 700 psig (4826 kN/m²), by means of a back pressure regulator valve. The molar ratio of CO₂/H₂S/H₂ in the feed mixture is 1/8/4. The crude product mixture is passed at atmospheric pressure by means of heated 316 stainless steel tubing to the heated gas sampling device of a gas chromatograph for analysis. Conversions and yields of the CO₂ to MM are calculated from the GC analysis.

The results, summarised in Table 6 below, show that CO₂ is likewise converted to MM, but that it is 35 somewhat slower to react and gives lower conversions to MM per pass than carbon monoxide does at the same reaction conditions.

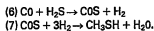
TABLE 6

40	CO ₂ Space	Preheater	Catalyst	CO ₂ /H ₂ S/H ₂	Pressure	Avg. %		40
	Velocity	Temp., °C	Temp., °C	Molar ratio	kN/m ²	Conversion	Avg. %	
						CO ₂ →MM	Yield	
							CO ₂ →MM	
45	5	185	271	1/8/4	4826	49	87	45
	5	170	290	1/8/4	4826	46	82	
	5	160	290	1/8/4	4826	52	92	
50	60	170	293	1/8/4	4826	24	58(*)	50

(*) Major by-products are CO and COS, which at lower space velocity 5 are apparently converted further to MM.

55 The above Examples 1-6 show the ability of the process of this invention to be used in a continuous manner at commercially feasible reaction conditions to produce methyl mercaptan from carbon monoxide and carbon dioxide with high conversions and yields.

When the preferred carbon monoxide is used as the starting material, gas chromatographic analyses of 60 the crude product streams show carbon dioxide to be the major by-product, with small amounts of carbonyl sulfide and dimethyl sulfide and traces of methane also detected. Methane formation is minimised by maintaining the reaction temperature below about 300°C. The remaining by-products are easily separated by distillation. In no case is methanol detected to be present in the crude product stream, indicating that it is not an intermediate in this process. The reaction sequence by which carbon monoxide is converted to MM thus 65 is as follows:



Reactions 6 and 7 proceed readily with the preferred catalyst and conditions of this process, whereas CO and H₂ do not react to produce methanol at these conditions.

The use of an alkali metal promoted zinc chromite in the process of this invention is particularly preferred as illustrated by the following example:

Example 7

The catalyst is prepared by impregnating a zinc chromite/alumina ($\text{Zn}(\text{CrO}_2)_2/\text{Al}_2\text{O}_3$) hydrogenation catalyst (Harshaw's Zn-0601 : ZnO 38%, Cr_2O_3 25% on activated alumina; average bulk density 97 lbs/cu.ft (15.52 g/cc), surface area 56 m²/g and pore volume 0.18 cc/g.) with aqueous cesium hydroxide followed by drying to deposit in the catalyst 10% by weight of cesium hydroxide. The catalyst/promoter is then sulfided by passage of gaseous hydrogen sulfide over the catalyst at elevated temperature until water of reaction is no longer detected in the gas stream.

Following preparation of the catalyst this was used as follows:

Molten sulfur was vaporized in a preheater and the sulfur vapour mixed with carbon monoxide and hydrogen sulfide to provide a gaseous feed mixture containing CO, S and H₂S in a molar ratio of 1:6:4. The gaseous feed mixture is passed continuously over the catalyst bed at a bed temperature of 395.6°C and at a reactor pressure of 250 psig (1723.75 kN/m²) and at a space velocity of 80 litres of CO per litre of catalyst per hour (at standard temperature and pressure).

Gas chromatographic analysis of the gas stream from the reactor show a 27.6% conversion of carbon monoxide to methyl mercaptan with total consumption of the sulfur content of the feed stream. By-product hydrogen sulfide produced in the reactor can be recycled.

CLAIMS

1. A process for the manufacture of methyl mercaptan which comprises continuously feeding to a reactor a vapour phase reactant mixture comprising a carbon oxide, hydrogen and either hydrogen sulfide or elemental sulfur, contacting the reaction mixture, in the vapour phase and at an elevated temperature and pressure with hydrogenation catalyst, recovering from the reactor a gaseous product stream, and separating from the product stream the product methyl mercaptan, wherein there is used a single phase solid catalyst prepared by:

A. mixing:

(1) an oxide, sulfide, hydroxide or salt of a metal or metals selected from iron, nickel, chromium, cobalt, molybdenum and zinc, with

(2) at least one compound selected from

(a) organic amine bases, namely aliphatic, cycloaliphatic, saturated heterocyclic, and aromatic amines having greater than 6 carbon atoms in each aliphatic, cycloaliphatic or aromatic radical, and

(b) alkali metal inorganic bases, namely alkali metal oxides, hydroxides, sulfides and salts; and then

B. at least partially sulfiding the admixture of A by heating the admixture in the presence of hydrogen sulfide or elemental sulfur; with the proviso that step B is optional when components A(1) and A(2) are both metal sulfides.

2. A process according to claim 1, wherein the catalyst is a single phase, solid composition comprising (a) a metallic sulfide or mixture of metallic sulfides selected from sulfides of iron, nickel, chromium, cobalt, molybdenum and zinc and

(b) an alkali metal sulfide or hydrosulfide.

3. A process according to claim 1 or 2, wherein component A(1) of the catalyst comprises a support.

4. A process according to claim 3, wherein the support is activated alumina.

5. A process according to any one of the preceding claims, wherein the carbon oxide is carbon monoxide or carbon dioxide.

6. A process according to any one of the preceding claims, wherein component A(2) is tridodecylamine.

7. A process according to any one of claims 1-6, wherein component A(2) is an oxide, hydroxide, sulfide or salt of potassium, rubidium or cesium.

8. A process according to any one of the preceding claims, wherein the reactants are a carbon oxide, hydrogen sulfide and hydrogen which are fed to the reactor in a molar ratio of from 1/3/2 to 1/8/3.

9. A process according to any one of claims 1-7, wherein the gaseous feed mixture contains elemental sulfur which reacts with the hydrogen *in situ* in the reactor to provide conversion to hydrogen sulfide.

10. A process according to claim 9, wherein the molar ratio of carbon oxide, elemental sulfur and hydrogen with respect to one another charged to the reactor is from 1/3/3 to 1/8/10.

11. A process according to any one of the preceding claims, wherein the temperature within the reactor is maintained within the range 250°C to 350°C, and the pressure within the reactor is maintained within the

range of from 4137-6894 kN/m².

12. A process according to claim 11, wherein the process is operated at conditions to provide a space velocity within the range of 5 to 200 volumes of carbon oxide per volume of catalyst per hour.

13. A process according to any one of the preceding claims, wherein the reactants are preheated to a temperature of at least 180°C.

14. A process according to any one of the preceding claims, wherein the metal of component A(1) is nickel.

15. A process according to claim 14, wherein component A(1) is a nickel oxide.

16. A process according to claim 14 or 15, wherein the nickel compound comprises from 5% to 20% by weight of the total catalyst, including the support, after sulfiding.

17. A process according to claim 14, 15 or 16, wherein component A(2)(b) is cesium hydroxide.

18. A process according to any one of claims 1-13, wherein the metal of component A(1) is zinc.

19. A process according to claim 18, wherein component A(1) comprises both zinc and chromium.

20. A process according to claim 19, wherein component A(1) is zinc chromite.

21. A process according to claim 1, substantially as hereinbefore described in any of the foregoing Examples.